



Effect of temperature, steam-to-carbon ratio, and alkali metal additives on improving the sulfur tolerance of a Rh/La–Al₂O₃ catalyst reforming gasoline for fuel cell applications[☆]

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ABSTRACT

2 wt% Rh/La–Al₂O₃ was tested for autothermal reforming (ATR) of S-free and 34 ppm-S-gasoline and characterized by scanning electron microscopy, elemental analyses, surface area, CO chemisorption, DRIFTS and X-ray absorption spectroscopy. The poisoning effect of S was more pronounced during ATR at 700 °C than at 800 °C. Complete recovery of the initial activity could be achieved when switching from S-containing gasoline to S-free gasoline at 800 °C, while only 50% of the activity could be recovered at 700 °C. Sulfur increased Rh sintering due to an increase in the catalyst temperature caused by a greater inhibition of steam reforming than partial oxidation. An increase in the H₂O:C from 2.0 to 3.0, or the addition of K to Rh significantly enhanced the sulfur tolerance of the catalysts. The beneficial effect of temperature, steam, and alkali metal was attributed to the inhibition of coke, which was the major cause of catalyst deactivation.

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1. Introduction

Reforming which includes partial oxidation, steam reforming, or autothermal reforming (ATR) of infrastructure fuels such as natural gas, liquefied petroleum gas, gasoline, or diesel, is one approach being investigated for producing H₂ for use with distributed fuel cell systems. For automotive fuel cell systems, reforming gasoline either on-board the vehicle or at the service station (“forecourt” concept) are also being considered. One challenge in reforming gasoline is the presence of sulfur, a known catalyst poison [1]. Although the concentration of sulfur in gasoline in the U.S. is decreasing, from an average of 150 ppm in 1998 to 30 ppm in 2007, the concentration is still high enough to degrade catalyst performance [2]. During reforming, the sulfur, which is initially present as organosulfur compounds, is converted primar-

ily to H₂S. The hydrogen sulfide is regarded as the primary sulfur poison for Ni reforming catalysts [3]. While Ni-based catalysts are used almost exclusively in the commercial production of H₂ via steam reforming of natural gas (often referred to as SMR for steam–methane reforming), most new catalysts being developed for reforming gasoline are based on precious metals because of their higher activity, better stability, and lesser tendency to deactivate due to coke formation. Although precious metals are more sulfur tolerant than Ni, they are still susceptible to poisoning by even low parts per million (ppm) concentrations of H₂S [1]. Studies suggest that H₂S adsorbs strongly and dissociatively on metal surfaces and that the adsorbed sulfur then prevents or modifies the further adsorption of reactant molecules [4].

There are several factors that affect the sulfur tolerance of catalysts, such as the reforming temperature, steam-to-carbon ratio, and the presence and amount of alkali and alkaline earth metals [5–8]. Alkali and alkaline earth metals, such as Ca is commonly used in commercial catalysts for SMR [9]. They neutralize acid sites which would catalyze coke deposition via the carbonium ion mechanism, and catalyze the gasification of the adsorbed carbon deposits, thus providing an *in situ* route for catalyst regeneration. The superiority of Rh compared to Pt or Pd for reforming of high-sulfur containing fuels has been reported in literature [10,11]. The purpose of the present study was to

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investigate the effect of temperature, the steam-to-carbon ratio, and the addition of K on the sulfur tolerance of Rh supported on a lanthanum-modified alumina catalyst for reforming low-sulfur (34 ppm by weight) gasoline.

2. Experimental

2.1. Preparation of catalysts

Rhodium was deposited on the oxide support using the incipient wetness technique. A sufficient amount of a solution containing rhodium nitrate ($\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$, Alfa Aesar, Johnson Matthey Co.) was added to $\text{La-Al}_2\text{O}_3$ (3.1 wt% La, HIQ X-160, 160 m^2/g , Alcoa World Alumina) to yield a 2 wt% loading of Rh. For the preparation of Rh–K, K nitrate (KNO_3 , J.T. Baker Chemical Co.) was co-impregnated together with Rh nitrate, to yield a 0.75 wt% loading of K, corresponding to a Rh:K molar ratio of 1. The Rh-supported oxide was then dried overnight at 100 °C and calcined by heating from room temperature to 700 °C at a rate of 5 °C/min and then holding at 700 °C for 1 h. The catalyst so produced is referred to as “as-prepared” in the discussion below.

2.2. Catalyst activity studies

Reforming studies were conducted to evaluate the activity and stability of a 2-wt% Rh/La– Al_2O_3 catalyst for the ATR of sulfur-free (<1 ppm S) gasoline or a low-sulfur (34 ppm S) California Tier II-type gasoline (both obtained from Chevron Phillips). Selected properties of these gasolines are shown in Table 1. These studies were conducted using a microreactor system. The microreactor system consisted of a 0.5-in. o.d. stainless steel tube heated by a temperature-programmed furnace, which was maintained at test temperatures ranging from 700 to 800 °C. The typical catalyst loading was 0.6 g of catalyst (sieved to –20/+40 mesh). The gasoline feed rate was 0.15 mL/min and the air feed rate was 415 mL/min (STP), providing an oxygen-to-carbon ($\text{O}_2:\text{C}$) ratio of 0.45. Four different water feed rates were investigated, 0.21, 0.28, 0.36, and 0.43 mL/min, providing steam-to-carbon ($\text{H}_2\text{O}:\text{C}$) ratios of 1.5, 2.0, 2.5, and 3.0, respectively. Based on the feed rates, the gas hourly space-velocities (GHSV) ranged from 43,000 to 62,000 h^{-1} . The temperature profile in the catalyst bed was measured using an Omega K-type multiprobe thermocouple with the probes separated by 0.25 in. Samples of the product gas were analyzed for H_2 , CO, CO_2 , and $\text{C}_1\text{--C}_8$ hydrocarbons using a gas chromatograph (Hewlett Packard Model 6890 customized by Wasson) equipped with a mass spectrometer.

2.3. Characterization

Hitachi S-4700-II field emission scanning electronic microscope (SEM), at Argonne's Electron Microscopy Center and JEOL 6400 SEM with Oxford INCA Energy Dispersive Spectrometer (EDS), at

the Analytical Chemistry Laboratory in the Chemical Sciences and Engineering Division at ANL, were used to detect the presence of carbon.

Elemental analyses for carbon and sulfur were performed using a combustion analysis technique (LECO) by the Analytical Chemistry Laboratory at ANL.

The BET surface areas of the catalysts were determined by N_2 adsorption using a commercial instrument (Micromeritics ASAP 2010). The catalysts were degassed by heating at 120 °C under vacuum prior to measuring the surface area.

Rh dispersion was measured by CO chemisorption using a commercial catalyst characterization system (Zeton Altamira, Model AMI-100) equipped with a thermal conductivity detector to detect CO uptake. The amount of sample used was ~50 mg. Prior to measuring the CO uptake, the samples were reduced in a flowing gas mixture of 3% H_2 in Ar by heating from ambient temperature to either 300 or 700 °C at a rate of 5 °C/min, and then flushed and cooled to ambient temperature in flowing He. The CO uptake measurements were conducted at 30 °C by injecting pulses containing 53 μL of CO into He flowing at a rate of 25 mL/min over the sample and measuring the amount of CO absorbed per pulse. For samples that had been evaluated for reforming gasoline, the samples were also pretreated in O_2 prior to making the CO dispersion measurement to remove any carbon that had deposited on the surface during reforming. The O_2 pretreatment involved heating the catalyst in a gas mixture of 4% O_2 in He from ambient temperature to 300 °C at a rate of 30 °C/min, then switching to helium while holding the sample at 300 °C for 30 min and allowing the sample to cool to ambient temperature.

X-ray absorption spectroscopy was conducted at the Advanced Photon Source at Argonne National Laboratory. Catalyst samples consisting of ~60 mg of material were pressed into thin self-supporting wafers and mounted in a cylindrical holder. The amount of catalyst used was chosen to optimize the edge step versus support absorbance. Samples were reduced in a flowing gas mixture consisting of 4% H_2 in Ar at 200 °C for 30 min and then cooled to room temperature prior to analysis. Spectra were recorded in the transmission mode using a cryogenically cooled double-crystal Si (1 1 1) monochromator with a platinum-coated mirror to minimize the presence of harmonics. The monochromator was scanned continuously from 23,060 to 24,250 eV with data points integrated over 1 eV for 0.05–0.10 s per data point. A Rh foil was used for energy calibration. The data were analyzed using ATHENA to remove the background, FEFF6 to model EXAFS data, and ARTEMIS to fit the EXAFS function [12,13]. For each spectrum, the Fourier transform of k^2 -weighted EXAFS oscillations was obtained using a Hanning-type window in the intervals $k = 2.5\text{--}15 \text{ \AA}^{-1}$. The backscattering amplitude of the nearest neighbor Rh–Rh contribution was taken from Rh foil and RhO_2 , assuming a co-ordination number of 12 for the first shell of Rh metal with a Rh–Rh distance of 2.69 Å, and a co-ordination number of 6 for the first shell of RhO_2 with a Rh–O distance of 1.96 Å. The quality of the fit was based on the *R*-factor, which is proportional to the sum of the squares of the difference between the model and the experimental data. For a good fit, the *R*-factor should be less than 0.02.

Diffuse reflectance infrared spectroscopy was performed on a Bomem DA3 spectrometer equipped with a Harrick Scientific HVC-DRP low pressure, high temperature diffuse reflectance cell. Infrared radiation was produced by a Globar source. The reflected radiation was collected by a prying mantis optical attachment (Harrick DRA-2CE) and re-directed to a mercury–cadmium–telluride detector (Bomem). For CO adsorption, 1000 ppm CO in N_2 was used. The feed (100 sccm) was forced to diffuse down flow through about 100 mg of sample (one-fourth of sample mixed with

Table 1
Properties of sulfur-free and low-sulfur gasolines

	S-free gasoline	Low S-gasoline
Specific gravity (60/60 °F)	0.7443	0.7414
Carbon (wt%)	86.8	Similar
Hydrogen (wt%)	13.2	Similar
Sulfur (ppm)	<1	34
Composition (vol.%):		
Aromatics	32.3	27.5
Olefins	0.8	5.0
Saturates	66.9	67.0

Analyses provided by Chevron Phillips.

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